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## **TESTING THE EFFECTIVENESS OF SPILL-TREATING AGENTS: LABORATORY TEST DEVELOPMENT AND INITIAL RESULTS**

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### **ABSTRACT**

Laboratory effectiveness tests have been developed for four classes of spill treating agents; solidifiers, demulsifying agents, surface-washing agents and dispersants. Many of the currently-available treating agents in these four categories have been tested for effectiveness. These results are presented.

Solidifiers or gelling agents change liquid oil to a solid. Tests show that these require a large amount of agent to solidify oil - ranging between 16% by weight, to over 200%. Demoussifiers or emulsion breakers are used to prevent or reverse the formation of water-in-oil emulsions. A newly-developed effectiveness test shows that only one product is highly effective, however many products will work, but require large amounts of spill treating agent.

Surfactant-containing materials are of two types, surface-washing agents and dispersants. Testing has shown that an agent which is a good dispersant is conversely a poor surface-washing agent, and vice versa. Tests of surface washing agents show that only a few agents have effectiveness of 25 to 40%, where this effectiveness is defined as the percentage of oil removed from a test surface. Extensive work has been done on dispersant testing and comparison of laboratory tests. All laboratory tests will yield the same effectiveness value if the oil-to-water ratio is about 1:1000 or greater, and if a settling time of 10 or more minutes is employed. Extensive results using the "swirling flask" test are reported. Heavy oils show effectiveness values of about 1%, medium crudes of about 10%, light crude oils of about 30% and very light oils of about 90%.

### **INTRODUCTION**

A large number of chemical agents for treating oil spills have been promoted in the past 20 years. In seventeen years, Environment Canada tested over 100 dispersants for toxicity and effectiveness. Only 8 products still remain on the accepted list. The compendium on oil spill treating agents prepared for the American Petroleum Institute in 1972 lists 69 dispersants and 43 beach clean-up agents, most of which are also listed as dispersants (American Petroleum Institute, 1972). Only two of these are current commercial products, but both are produced in different formulations. Over 60 biodegradation agents, including bacterial mixtures, enzymes or fertilizers have been proposed and only 12 of these, all very recent inventions, remain on the market. Over 100 surface washing agents have been sold in the North American market. About 12 of these are still commercially available. A number of agents which have been sold for various purposes, but do not fit into the above categories, include those that help trace or detect an oil, those which are combinations of the categories described above, and those very vague items that are claimed to make oil disappear, become non-toxic, etc.

It is estimated that over 100 of these agents has been promoted at one time or another on the North American market. The total number of agents proposed world wide is estimated to be 600, of which only about 100 were ever tested in the lab or field, even in a limited way. The high level of activity causes difficulties to the potential buyer and to the environmentalist because they are unable to discriminate between those products which will actually help the situation and those which can cause further damage.

Effectiveness will remain the major problem with most treating agents. Effectiveness is generally a function of oil type and composition. Crude and refined oil products have a wide range of molecular sizes and composition including whole categories of materials like asphaltenes, alkanes, aromatics and resins. What is often effective for small asphaltene compounds in the oil may be ineffective on the large asphaltenes. What is effective on an aromatic compound may not be effective on a polar compound. Additionally, the composition of crude oils varies widely. This leaves little scope for a universally-applicable and effective spill control chemical.

Testing of spill treating agents has involved two facets at Environment Canada, the first being testing for toxicity and other forms of environmental acceptability, and the second is effectiveness testing. Criteria for selection of test methods include; similarity to actual field test results and conditions, reproducibility of results, simplicity of apparatus and procedure, and correlation of results with those from other tests. A number of projects have been initiated to develop tests and to complete testing of most spill treating agents currently being sold.

## **GELLING AGENTS OR SOLIDIFIERS**

Gelling agents are those agents which change oil from liquid to solid. Also known as solidifiers, these agents often consist of polymerization catalysts and cross-linking agents. Agents which are actually sorbents are not considered to be gelling agents. Three solidifiers were tested by Environment Canada in the past:

1. The BP (British Petroleum) product which consisted of deodorized kerosene and a cross-linking agent,
2. A Japanese product consisting of an amine which forms a polymer, and
3. The solidification agent proposed by Professor Bannister of the University of Lowell, an agent which used liquefied carbon dioxide and an activating agent.

During tests conducted in the laboratory, all three agents functioned, but required large amounts of agent to effectively solidify the oil. Under some situations the oil became a viscous semi-solid which would not aid in recovery. The BP agent worked better than the other agents and was tested in larger scale by the Canadian Coast Guard and the Canadian oil industry. In these large scale tests even more agent was required to solidify the oil, in fact up to 40% of the actual volume of the oil itself. This is double the laboratory requirement. Both requirements were deemed to be far in excess of what was actually practical in the event of a real spill. Because of the large amount of agent required, gelling agents have not been historically used nor stocked for use by spill responders.

A standard test was developed to assess new solidifiers. The test consists of adding solidifier to an oil while being continuously stirred until the oil is solid. An outline

of the procedure is given in the Appendix. The test results are repeatable within 5%. Results of testing some solidifiers is given in Table 1. Values are given as the weight percent of the agent required to solidify an oil completely.

**TABLE 1 SOLIDIFIER TEST RESULTS**

<u>Product Name</u>	<u>Percentage To Solidify</u>
Rawflex	16
Norsorex	19
Oil Bond 100	33
Oil Sponge	36
Petro Lock	44
Molten Wax	109
Powdered Wax	278

### **DEMOUSSIFIERS OR EMULSION BREAKERS**

A number of agents were also available to break or prevent emulsions. Most agents were hydrophilic surfactants, that is surfactants with an strong tendency to make oil-in-water emulsions. Such surfactants have the ability to reverse the water-in-oil emulsion to two separate phases. The problem with a hydrophilic surfactant is that it is more soluble in water than in oil and will quickly leave the oil. Obviously such products cannot be successfully used on open water. Some recent products avoided this problem by using a less water-soluble surfactant and accepting the resulting decrease in effectiveness. One recent product, "Demoussifier", developed by Environment Canada does not use surfactant in the normal sense of the word. This product does not suffer the limitations noted above.

Two commercial products, Exxon Breaxit and the Shell product, LA 1834 and a surfactant, sodium dioctyl sulfosuccinate were evaluated in one study (S.L. Ross Environmental Research, 1986). All three products functioned in a limited way, but only the Shell product prevented the formation of emulsions over a wide range of oils and conditions. The Shell product and the Exxon product are not commercially available, but have been obtainable in small quantities for testing.

The United States Minerals Management Service and Environment Canada joined forces to evaluate Demoussifier, an emulsion breaker and preventer. Results of the extensive testing on this product have been widely published (Fingas and Tennyson, 1988; Bobra et. al., 1988a, 1988b; Seakem, 1990).

Demoussifier was developed at Environment Canada's River Road Environmental Technology Centre and functions both to break emulsions and prevent their formation. Demoussifier was tested on a large scale using the Esso test tank in Calgary, Alberta. The demoussifier prevented the formation of water-in-oil emulsions and did so at treatment ratios as low as 1:2000 (500 ppm). The product was then tested on a large scale offshore. The Demoussifier trials were performed by laying down a five-barrel oil slick, treating it with the product at the specified ratio, taking samples at subsequent intervals and measuring the water content and the viscosity. One slick was left untreated and then treated at the 240-minute interval to test Demoussifier's ability to break emulsion

at sea. A large reduction in viscosity (105,000 to 22,600 cSt) occurred over the 30-minute sampling period, showing that the product worked well to break the emulsion. The product continued to work well over the five-hour test period to prevent the formation of emulsions.

A new laboratory test is under development at Environment Canada. The test is intended to provide a fast, convenient means of assessing emulsion preventers and breakers. Preliminary results of tests of some products is given in Table 2. The minimum operative concentration is defined as the lowest concentration at which the emulsion volume is reduced to half its initial value. The percent emulsion reduction is the percentage reduction in emulsion volume at a treating-agent concentration of 5000 ppm. The products tested included only one specifically intended for emulsion breaking. The others are dispersants or common household cleaners. Two products, Demoussifier and the dispersant Dasic Slickgone, show good performance in these preliminary tests.

<b>Table 2 Preliminary Test Results on Emulsion Breakers</b>		
<u>Agent</u>	<u>Minimum Operative Concentration(ppm)</u>	<u>% Emulsion Reduction at 5000 ppm</u>
Demoussifier	<1000	65
Dasic Slickgone	1000	69
Palmolive	6000	21
Enersperse 700	20000	21
Corexit CRX-8	40000	45
Corexit 9527	40000	42
Mr. Clean	inoperative	1

### **SURFACE-WASHING AGENTS**

The most common and most promoted treating agents are those containing surfactants as the major ingredient. These agents have been divided into two groups, dispersants and surface-washing agents. Dispersants are those agents which have approximately the same solubility in water and oil and will cause the oil to be dispersed into the water in the form of fine droplets. Surface-washing agents are those agents which remove oil from solid surfaces such as beaches by a mechanism known as detergency. As it turns out, the mechanism of dispersancy and detergency are quite different and testing has found that a product which is a good surface-washing agent is a poor dispersant and vice versa.

A test for surface-washing agents was developed by Environment Canada and a number of commercial products have been tested using this protocol. A summary procedure is given in the Appendix. The test measures how much oil is removed from a standard test surface when the surface-washing agent is allowed to soak into the oil and then rinsed with water. Table 3 shows the results of these tests with a seawater rinse and the results of an aquatic toxicity test (lethal concentration to half of the test population of Rainbow Trout over four days in mg/L; larger values indicate less toxicity) and a dispersant effectiveness test (swirling flask test, values represent percent oil put into the water column) for the same products. This latter data point was included to show the

opposite nature of dispersant and surface-washing effectiveness. Low dispersant effectiveness is a benefit for any product that will be used as a surface washing agent because oil can then be recovered rather than dispersed into the water column. Furthermore, because the two properties of surface-washing and dispersancy are orthogonal, highly effective products do not have a significant dispersant effectiveness. Some products display neither property.

**TABLE 3 SURFACE-WASHING AGENT TEST RESULTS**

<u>Agent</u>	<u>Percent Oil Removed</u>	<u>Toxicity</u>	<u>Dispersant Effectiveness(%)</u>
D-Limonene	52	35	0
Penmul R-740	44	24	9
Corexit 9580	42	> 5600	0
Formula 2067	39	11	0
Citrikleen XPC	36	34	2
Formula 861	32	24	0
Corexit 7664	27	850	2
BP 1100 WD	21	120	6
Re-Entry	17	8	0
Palmolive dish soap	16	13	9
Breaker 4	13	340	0
Nokomis 3	13	110	0
Citrikleen FC1160	12	75	0
Con-Lei	12	70	0
Sunlight dish soap	12	13	9
Citrikleen 1855	12	55	0
Con-Lei	12	70	0
Bioversal	11	120	0
Mr. Clean	6	30	0
Gran Control	6	75	0
Corexit CRX-8	5	2	48
Formula 730	5	33	0
Corexit 9527	3	108	41
Tornado	3	1350	0
Biosolve	2	9	0
Lestoil	1	51	0
Enersperse 700	1	50	56

## DISPERSANTS

Dispersants have generated the greatest amount of study and discussion of all spill treating agents. Initial concern was the toxicity of the product, but in recent years this focus has shifted to effectiveness.

Field tests of oil-spill dispersants have not been successful. Over the past 12 years, 107 test spills have been laid out to test the effectiveness of oil-spill dispersants (Fingas, 1989). Of the 107 slicks documented, 23 were controls used to establish a comparison.

Percentage effectiveness is reported in 25 spills and the average for these is 30%. Values range from 0 to 100%. Most experimenters have not assigned effectiveness values, because mass balances are nearly impossible to determine under field conditions. The test results show clearly that dispersants are not highly effective, even under highly controlled experimental situations. Of greater concern than this is the methodology used to estimate effectiveness. Some experimenters simply estimated effectiveness from visual appearances, but most based their measure on integrations of water column concentrations relative to surface slick dimensions. This is not a correct means to perform the measure because the underwater concentrations have little positional relationship to the surface slick. Underwater dynamics of the ocean are very different than surface dynamics. Extreme cases of the positional variances between surface and sub-surface slicks have been illustrated by Brown and Goodman in controlled tank testing (Brown and Goodman, 1988). Their work has shown that the underwater plumes move in highly random fashions with respect to the surface slick and even two trials conducted on the same day and in the same tank location proved that the plumes may not have similar movement patterns. Furthermore, all of the experimenters who used underwater concentrations to estimate field effectiveness also used the method of dividing the water into different compartments and averaging concentrations. Mathematically this is not appropriate and can result in effectiveness values that are very large. Because of these factors, underwater estimates of oil spill dispersant effectiveness are highly inaccurate and misleading. Surface measures are also inadequate at this time but may be possible with the development of new remote sensors (Goodman and Fingas, 1988).

A number of laboratory studies have been performed to compare the test results from different apparatus and procedures. A review of these results shows that there is poor correlation in effectiveness results between the various test methods when these methods are followed as written (Fingas, Bobra and Velicogna, 1987). A recent study by the present author has shown that lack of correlation is primarily a function of settling time allowed between the time that the energy is no longer applied and the time that the water sample is taken from the apparatus (Fingas et. al. 1989). Another important factor is the oil-to-water ratio used in the apparatus. When these two parameters are adjusted to be the same and to larger values, test results from most apparatus are similar. Results from more energetic dispersant effectiveness tests are higher but when corrected for natural dispersion, these results are nearly identical to those from less energetic apparatus. Given that essentially identical results can now be obtained from virtually any laboratory tests, a simple, repeatable and fast test can be chosen to make determinations of the dispersant effectiveness. One test developed by Environment Canada called the "swirling flask" test meets these criteria and has been used to test many combinations of oils and dispersants. A summary procedure of this test is given in the Appendix. Three variants of the test are invoked, one with the dispersant pre-mixed with the oil at a ratio of 1:25 (dispersant:oil), one with the dispersant applied as a single drop at an oil to dispersant ratio of 1:10, and as two drops applied at the same ratio. The pre-mixed test is the most-frequently used test because it yields the most repeatable results. The drop-wise tests are performed to measure the difference in performance when the dispersant is added dropwise versus pre-mixed. The difference between the two tests is a measure of how

well the dispersant mixes with the oil and the water. A major difference in performance between the pre-mixed and drop-wise test indicates that the dispersant mixes more readily with water rather than the oil. The two-drop test is a measure of the herding characteristics of the oil-dispersant combination. A dispersant which herds the oil will show a lower effectiveness in the two-drops test compared to that shown in the one-drop test. The second dispersant drop will land on clear water if herding has occurred with the first drop. The values in Table 4 are an average of all three test results.

**TABLE 4 DISPERSANT EFFECTIVENESS RESULTS**

Oil	Percent effectiveness with Dispersant			
	Corexit 9527	Corexit CRX-8	Enersperse 700	Dasic Slickgone
Alberta	33	45	51	24
Arabian Light	17	9	22	33
Avalon	11	5	11	16
Bent Horn	17	20	23	30
Bunker C	1	2	2	1
California heavy	1	1	1	1
Endicott	7	8	6	14
Endicott weathered	6	2	6	3
Hibernia	6	6	10	14
Hibernia weathered	4	3	8	7
Lago Medio	5	5	13	15
Norman Wells	36	43	51	26
Nuguini	50	57	55	28
Panuk	96	78	96	40
Prudhoe Bay	7	7	10	14
Prudhoe Bay weathered	4	4	8	10
South Louisiana	31	36	48	42
Synthetic crude	63	41	61	25
Transmountain	8	8	28	27
Used motor oil	33	31	36	29

A few trends are seen in these data. First, there is little difference between dispersants other than the slight tendency of Dasic to disperse heavier oils better than the other dispersants, but lighter oils to a lesser degree. Second, the average effectiveness for heavy oils is about 1%, for medium crudes about 10%, for light crudes about 30% and for very light oils about 90%. Finally, weathered oils are dispersed to a lesser degree than their fresh counterparts.

Toxicity of three of these dispersants was measured and these data are presented in Table 3.

## CONCLUDING REMARKS

Testing of spill treating agents shows that there exists clear differences in their effectiveness with different oils. Large differences in effectiveness also exist between many of the treating agents. The testing of effectiveness along with toxicity is an important screening tool for selecting treating agents.

## ACKNOWLEDGEMENTS

Funding for the studies was provided by Environment Canada and the United States Minerals Management Service.

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## **APPENDIX**     Summary Test Procedures

### 1. Solidifier Test

1.a. Equipment:     Stirrer     stop watch     analytical balance

1.b. Supplies:     Jar     ASMB(Alberta Sweet Mixed Blend) standard oil     saltwater  
                         spatula

1.c. Procedure:     200 mL of seawater is placed into jar and 20 mL of the standard oil is weighed and placed on the water. A stirrer is placed at the oil-water interface and is turned on. After one minute, quantities of the solidification agent are added at 1-minute intervals from a pre-weighed container. A plastic spatula is used to test the solidity of the oil. When the oil is solid, the weight of solidifier added and weight of the oil are used to calculate the percentage required to solidify.

### 2. Preliminary Emulsion Breaker Test

2.a. Equipment:     Wrist-action shaker     vernier callipers     stop watch

2.b. Supplies:     500 mL graduated cylinder     salt water     test oil(half Bunker C and half ASMB weathered 7.7%)     pipettes

2.c. Procedure:     Place 400 mL water in the cylinder and 1 mL oil on the surface of this water. Place the oil in the shaker and shake through an angle of 2 degrees for a period of 40 minutes. Stop the shaker and measure the height of the emulsion with the callipers both along the shaking axis and perpendicular to it. The height of the emulsion is taken as the average of these two numbers. The treating agent is added and the cylinder shaken for another 60 minutes. The height of the emulsion is taken again and used to calculate the percentage reduction for that quantity of treating agent. The minimum quantity is taken as the concentration of agent that cause a 50% reduction in emulsion height.

### 3. Surface-Washing Agent Test

3.a. Equipment: analytical balance    stainless steel trough (3/4 in. angle iron)

3.b. Supplies: test oil (Bunker C)    pipettes    50 mL syringe    tissue    tweezers

3.c. Procedure: Place 0.15 mL of the test oil onto a 50 mm strip in the centre of the trough. Let the oil stand for 10 minutes and then weigh the oil and trough. Apply 0.03 mL of the surface washing agent to the oil and distribute it along the test oil strip.

Let the material soak for 10 minutes. Place the trough in a stand at 15 degrees from horizontal and using the 50 mL syringe with a 18 gauge needle as a funnel, flush the surface with 5 mL water. Let stand for another 10 minutes and flush again with the same amount of water. Let dry for 10 minutes and carefully remove any remaining water droplets with tweezers and a tissue. Weigh the trough to determine the weight of oil removed.

### 4. Dispersant Test (Swirling Flask Procedure)

4.a. Equipment: laboratory shaker    spectrometer

4.b. Supplies: 125 mL Erlenmeyer flask with bottom spout    test oil    pipettes  
                         salt water    separatory funnels    graduated cylinders

4.c. Procedure: Place 120 mL of water into the test flask and float 0.1 mL oil/dispersant on the water. Shake the flask(s) for 20 minutes at 150 rpm. Let stand for a further 10 minutes and take a 30 mL sample through the side-spout. Extract the oil with 3 successive aliquots of 5 mL of dichloromethane. Read the absorbency of the combined dichloromethane extracts in a spectrophotometer at 340, 370 and 400 nm. Using a calibration curve, determine the percent effectiveness at each wavelength and average for the final result.

The one drop procedure is performed as above but the dispersant (0.01 mL) is applied to the centre of the oil, after it has been placed on the water. The two drop test is performed in similar manner but the first drop of dispersant (0.05 mL) is placed a point 1/3 across the diameter of the oil surface and the second drop 5 seconds later at the 2/3 point across the same diameter.

Calibration curves are prepared by adding the amount of oil calculated to yield a given percentage to 30 mL water and proceeding as though this were a regular run.